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(54) Title: POLYMERIC MATERIALS FOR PHOTOCHROMIC APPLICATIONS

(57) Abstract

A polymeric material comprising main chain ether groups or side chain alkoxylated groups that is effective as a carrier of photochromic additives. The polymeric material preferably has a glass trnsition temperature of at least 125 °F and a cross link density of 2 to 8 moles per liter, more preferably 2.5 to 6 moles per liter. When photochromic additives are incorporated in such materials, the speed of switching is maintained at a high level, while the level of photochromic response is rendered relatively insensitive to temperature changes. Examples of optical products into which such materials can be incorporated include ophthalmic lenses, goggles, safety glasses, windows, and windshields.

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POLYMERIC MATERIALS FOR PHOTOCHROMIC APPLICATIONS

This application is a continuation-in-part of U.S. Serial No. 08/435,126, entitled "Adhesive Photochromic Matrix Layers for use in Optical Articles," filed May 5, 1995, naming Amitava Gupta, Ronald D. Blum and Venkatramani S. Iyer as inventors. This application is also a continuation-in-part of Application Serial No. 08,167,103, entitled "Method and Apparatus for Manufacturing Photochromic Lenses," filed December 15, 1993, naming Amitava Gupta and Ronald Blum as inventors, which is a continuation-in-part of Application Serial No. 08/165,056, entitled "Method and Apparatus for Manufacturing Photochromic Lenses," filed December 10, 1993, also naming Amitava Gupta and Ronald Blum as inventors.

FIELD OF THE INVENTION

This invention relates to thin layers of materials which function as effective carriers for photochromic additives, can be attached to many types of optical substrates (including ophthalmic lenses, semifinished lens blanks, optical preforms, goggles, safety glasses, windows, and windshields), and can be encapsulated between two layers of such optical products, at least one of which is transparent to ultraviolet radiation.

BACKGROUND OF THE INVENTION

It is often desirable to incorporate photochromic properties into optical products which are used both in sunlight and in darkness. This allows such products to develop a dark tint that serves to reduce outdoor glare during exposure to sunlight, while also allowing them to turn clear when sunlight is not present. A combination of three or more photochromic additives, each with a colored state absorbing in a particular part of the visible wavelength range (400- 750 NM) is usually used to obtain a neutral gray or brown tint.

While photochromic ophthalmic lenses have been successfully commercialized for many years, photochromic versions of other optical products, such as windshields, windows, goggles and safety glasses, are not yet in common use, because it is difficult and expensive to manufacture photochromic versions of these products.

Certain constraints also have to be imposed on the physical properties of materials, particularly plastic materials, in order to enable photochromic additives incorporated in them to perform their intended function (i.e., switch from a clear state to a dark state in presence of sunlight, and return to a clear state when exposure to sunlight ends). These constraints compromise the structural and optical performance of these materials, and can render them unsuitable for their intended applications.

It is useful to review the mechanism by which photochromic additives are believed to perform, in order to further understand the deficiencies of currently available photochromic materials, and to understand the design rationale for layers bearing photochromic additives.

Photochromic molecules exist in two ground state configurations ("doublet ground states"), one of which does not absorb visible radiation at any significant level, the other of which is able to absorb visible

radiation strongly. Each of these ground state configurations has a corresponding electronically excited state, as shown in Figure 1. The four state diagram of a typical organic photochromic molecule shown in Figure 1 includes two ground states: a colorless state, 1, and a colored state, 2, which are thermally interconvertible. For certain photochromic materials, state 2 can be converted to state 1 through absorption of visible light. An excited state 3 formed by absorption of ultraviolet light by ground state 1 decays to form an excited state 4 and from excited state 4 decays to ground state 2. The excited state 3 also directly decays to ground state 2 (the activating process). The ground state 2 forms the excited state 4 which returns to both ground state 1 and ground state 2 on deactivation (the bleaching process), as shown in Figure 1. The activated conversion of ground state 2 into ground state 1 introduces a temperature dependence into the dynamic range of the photochromic response of organic photochromic materials. Thus, the higher the temperature, the faster the conversion of ground state 2 into ground state 1, and the equilibrium population of ground state 2 decreases relative to the population of ground state 1. Accordingly, upon activation, the higher the temperature, the more photochromic additive exists in the colorless form 1.

Raising the temperature barrier between ground state 2 and ground state 1 slows down the rate of conversion of ground state 2 into ground state 1, and hence lessens the reduction of the photochromic response ("Activation Level") on raising the temperature. At the same time, however, it slows down the speed of switching of the photochromic additive to the transparent state once it is removed from sunlight exposure.

The photochromic materials available in the state of the art, therefore, represent a compromise between the switching speed (measured as time required for the

photochromic material to return to the colorless form when solar exposure is terminated, also referred to as the rate of the bleaching process) and the temperature dependence of the dynamic range of the photochromic response (measured by the population of the colored form relative to the colorless form at thermal equilibrium when being exposed to solar or ultraviolet radiation at any particular temperature, also referred to as the level of activation).

For example, U.S. Patent No. 5,110,881, issued to McBain, describes a plastic material in which this trade-off is shifted towards a better level of activation at a higher temperature, but the resulting switching (bleaching) rate is more than 5 minutes at 72°F, measured as $T_{0.5}$, the time needed to regain 50% of the optical transmission lost when exposed to sunlight or ultraviolet radiation ("Plastic Photochromic Eyewear: A Revolution", C.N. Welch and J.C.Crano, PPG Industries Inc.)

A third deficiency of currently available photochromic materials is that such materials are generally made by diffusing or infusing ("imbibing") photochromic additives into bulk plastic materials, or by incorporating the photochromic additives into a monomer or monomers, and subsequently polymerizing the monomer formulation to form the bulk plastic material (see, e.g., U.S. Patent No. 4,909,963 issued to Kwak and Chen, U.S. Patent No. 4,637,698 issued to Kwak and 8Hurditch, and U.S. Patent No. 5,185,390 issued to Fischer).

SUMMARY OF THE INVENTION

In view of the above, it is an object of this invention to develop plastic materials which incorporate photochromic additives in which the speed of switching is maintained at a high level, while the level of photochromic response is rendered relatively insensitive

to temperature changes. It is a further object of this invention to develop optical products (including but not limited to ophthalmic lenses, goggles, safety glasses, windows, and windshields) incorporating these materials that are simple and inexpensive to make and whose structural and optical performance are not significantly compromised.

According to an embodiment of the invention, a polymeric material comprising main chain ether groups or side chain alkoxylated groups is provided that is effective as a carrier of photochromic additives. The polymeric material preferably has a glass transition temperature of at least 125°F and a cross link density of 2 to 8 moles per liter, more preferably 2.5 to 6 moles per liter. The polymeric material preferably comprises one or more polymerized monomers selected from the group consisting of one or more mono- or multi-functional acrylates or methacrylates. Examples include bisphenol A derivatives of mono- or multi-functional acrylates or methacrylates; aromatic carbonates of mono- or multi-functional acrylates or methacrylates; aliphatic carbonates of mono- or multi-functional acrylates or methacrylates; and allyl and vinyl derivatives of mono- or multi-functional acrylates or methacrylates. Further examples include polyethylene glycol diacrylates, ethoxylated bisphenol A diacrylates, 2-phenoxyethyl methacrylates, alkoxylated trifunctional aliphatic acrylates, alkoxylated aliphatic diacrylate esters, tetrahydrofurfuryl acrylates, alkoxylated trifunctional acrylates, and alkoxylated difunctional acrylate esters.

According to another embodiment of the present invention, resin formulations containing monomers which can be cured to form polymeric materials, such as those discussed above, are provided. Examples of such monomers are discussed above. The resin formulations of the present invention preferably comprise either a

photoinitiator or a thermal initiator. Preferred photoinitiators include bisdimethoxybenzoyl trimethylpentyl phosphine oxide, 1-hydroxy cyclohexyl phenyl ketone, and 2-hydroxy, 2-methyl, 1-phenyl propane. Preferred thermal initiators include organic peroxides, hydroperoxides, percarbonates, peracetates and azo derivatives. The resin formulations of the present invention can also include additional additives, such as antioxidants. Preferred antioxidants include thiodiethylene bis(hydrocinnamide) and bis (1,2,2,6,6,-pentamethyl-4-piperidyl sebacate). One or more photochromic additives can also be included in the resin formulations of the present invention. Preferred photochromic additives include spiro(indolino)naphthoxazines, spiro(indolino)pyridobenzoxazines, spiro(benzindolino)naphthoxazines, and octamethyl stilbene.

Optical products can be made from either the above polymeric material or the above resin. Optical products appropriate for the practice of the present invention include uncorrected lenses, ophthalmic lenses, semifinished lens blanks, optical preforms, goggles, safety glasses, windows, and windshields.

Other embodiments of the present invention relate to methods of forming a polymeric material that is impregnated with a photochromic additive. According to a first embodiment, the photochromic additive is incorporated into the polymeric material by adding the photochromic additive to a monomer formulation before it is polymerized.

According to a second embodiment, the photochromic additive is incorporated into the polymeric material by diffusing the photochromic additive material into the polymeric material. This can be accomplished in a variety of ways. For example, the photochromic additive can incorporated into the polymeric material by

immersing it into a solution of the photochromic additives in a chemically inert solvent, by spraying or spin coating the polymeric material with a solution of the photochromic additives in a chemically inert solvent, by repeatedly providing a surface layer of polymeric material and subsequently incorporating the photochromic additive into the surface layer of polymeric material, and so forth.

The polymeric material, either with or without the incorporated photochromic additive, can be adhered to an optical product, for example, by an interfacial region composed of an interpenetrating network, by an adhesive layer, and so forth.

Another way by which the polymeric material incorporating the photochromic additive can be included in an optical product is by forming the polymeric material incorporating the photochromic additive as a solid powder, suspending the solid powder in a liquid, and applying the suspended powder to an optical product. Yet another way of including the polymeric material incorporating the photochromic additive into an optical product is by partially polymerizing the polymeric material; loading the partially polymerized polymeric material with the photochromic additives; dispersing the loaded, partially polymerized polymeric material in a carrier fluid; and applying the carrier fluid with the dispersed, loaded, partially polymerized polymeric material onto an optical product.

Still other objects and advantages of the invention and alternative embodiments will readily become apparent to those skilled in the art, particularly after reading the detailed description and claims set forth below.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a four state diagram of a typical organic photochromic molecule.

DETAILED DISCUSSION OF THE INVENTION

Referring to the above discussion in connection with Figure 1, but without wishing to be held to any particular theory or theories of operation, it is clear that the rate of conversion of ground state 2 into ground state 1 controls the level of activation as well as the switching (bleaching) speed. Thus, the faster the conversion of ground state 2 into ground state 1, the lower the level of activation, but the faster the bleaching rate. For slow bleaching systems, the level of activation is controlled by the second process of conversion of ground state 2 into ground state 1, i.e., through absorption of visible light by ground state 2, and subsequent deactivation to form 1, as shown in Figure 1. For such slow switching materials, the level of activation approaches a maximum, but the bleaching rate is slow.

In several photochromic molecules, the bleaching rate provided by the photochromic molecule itself is much faster than the bleaching rate permitted by the segmental rotational rates of the plastic matrix constituting the optical product. Therefore, the bleaching rate is very largely determined by the nature of the matrix, in particular its segmental rotational rate. As a result, the level of activation is also largely determined by the nature of the matrix for these photochromic molecules. Such photochromic molecules are disclosed, for example, in U.S. Patent No. 5,349,065, issued to Tanaka, Tanaka and Kida, or U.S. Patent No. 5,021,196, issued to Crano, Kwiatkowski and Hurditch. Plastic products incorporating such molecules exhibit matrix dependent bleaching rates and activation levels.

A series of polymeric matrices were developed by the present inventors for use in conjunction with such photochromic molecules that are capable of achieving high levels of activation at temperatures up to and

exceeding 100°F, and still retain bleaching rates ($T_{0.5}$) of less than 1 minute at room temperature (70°-90°F).

A key feature of the polymeric matrices of the present invention is that the barrier to conversion of ground state 2 into ground state 1 (Figure 1), presented by the polymeric segments, contains a component which is weakly dependent on temperature, i.e., it remains nearly constant over the temperature range of 70°F - 100°F. This is accomplished by selecting appropriate monomers which, after curing, contain constituents (either at side chains or at main chains) capable of undergoing rotation with a very low activation energy (less than 40 kJ/Mol). A combination of such constituents are provided so that the polymeric network has several degrees of freedom of rotational motion available to it. At the same time the network is cross linked to ensure that the absolute magnitude of the rotational frequency remains restricted. This is done to ensure that the rate of conversion of ground state 2 into ground state 1 does not become excessively fast. Otherwise, the level of activation will become unacceptably low at the upper limit of the target temperature range (105°F). Generally speaking, the segmental mobility of polymeric matrices increases 5 fold or more when the ambient temperature is at or above its glass transition temperature. Accordingly, all matrices are formulated to have glass transition temperature well above the target temperature range (20°F or more), so that only local group or side chain motions are available to stimulate the conversion of ground state 2 into ground state 1 (Figure 1).

It was found that when monomers containing main or side chain ether groups (embodied in certain ethoxylated or propoxylated derivatives or methoxy substituents present as side chains) were used to formulate the polymeric matrix for incorporation of photochromic additives, the matrices permitted rapid conversion of

ground state 2 into ground state 1 in the absence of cross linking, or at low levels of cross link density. Such a matrix provided rapid bleaching rates, but low levels of activation at or near the upper limit of the target temperature range. As the cross link density was increased, the conversion rate of ground state 2 into ground state 1 was slowed down, simultaneously increasing the activation level at the temperature range 90°-100°F. A range of cross link density was found within which the activation level remained approximately constant (varying less than 30%) over a relatively wide temperature range (80°-100°F), leaving the switching speed (bleaching rate) also approximately unchanged at 30-45 seconds. It is believed that the polymeric matrices within this range of cross link densities and concentrations of ether groups present as alkoxy groups or side chains provide an optimum number of rotational degrees of freedom with low temperature dependence to a photochromic molecule incorporated in the matrix.

Thus, a combination of polyethylene glycol (400) diacrylate, ethoxylated bisphenol A diacrylate, 2-phenoxyethyl methacrylate, either used as a three component mixture or mixed with bisallyl ethylene carbonate, provide independent control of crosslink density and glass transition temperature of the resulting polymeric matrices, in addition to providing both main chain ether groups and side chain alkoxylated groups in the resulting network.

In addition to the monomers listed above, it is possible to use a series of polyethylene glycol diacrylates of different molecular weights, alkoxylated trifunctional aliphatic acrylates (such as SR9008, available from Sartomer Corp), and alkoxylated aliphatic diacrylate esters (such as SR9209, available from Sartomer Corp). In addition, other oligomeric mono- or multi-functional acrylates or methacrylates may also be used, provided that the range of cross link density does

not fall outside of 2-8 moles per liter, preferably 2.5-6 moles per liter. Preferable candidates among acrylates and methacrylates are those which bear either aliphatic or aromatic ether linkages on the main chain, such as Bisphenol A derivatives, or aromatic carbonates derived thereof, aliphatic carbonates, as well as side chain substitutions bearing alkoxy linkages. In addition, allyl and vinyl derivatives may be used, such as styrene, substituted styrenes, or bisallyl carbonate, or derivatives thereof.

The monomer formulation was typically photopolymerized using photointiators such as bisdimethoxybenzoyl trimethylpentyl phosphine oxide (BAPO, available from Ciba Geigy Corp), 1-Hydroxy cyclohexyl phenyl ketone (Irgacure 184, available from Ciba Geigy Corp), or 2-hydroxy, 2-methyl, 1-phenyl propane (Durcure 1173, available from Radcure Corp). Alternatively the monomer formulation may be thermally polymerized using an organic peroxide, hydroperoxide, percarbonate, peracetate, or an azo derivative as a thermal polymerization initiator. Examples are benzoyl peroxide, 2,2′ azobisisobutyronitrile, or diisopropyl percarbonate.

Antioxidants, such as thiodiethylene bis(hydrocinnamide) (Irganox 1035, available from Ciba Geigy Corp) or bis (1,2,2,6,6,-pentamethyl-4-piperidyl sebacate) (Tinuvin 292, available from Ciba Geigy Corp), may also be included in the monomer formulation.

Table 1 shows some typical formulations, and their glass transition temperatures. The formulations are custom developed for a given substrate material (e.g., an optical product made of CR-39 (Trademark of PPG Corp), polycarbonate of bisphenol A, or a polyurethane). In each case, the monomers are selected to develop strong bonding and compatibility with the substrate to which this matrix is to be applied.

Table 1 - List of Preferred Formulations for Certain Substrates

FORMULATION	MONOMERS	WEIGHT RATIOS (%)	GLASS TRANSITION TEMP	SUBSTRATE
1	DEG-BAC 9008 PEGDA 9209 184	70 4 9 15 2	80°C (176°F)	CR-39
2	DEG-BAC PEGDA 9209 184	70 15 13 2	65°C (149°F)	CR-39
3	DEG-BAC THFA 9209 184 TIN 1130 TIN 292	50 25 23 1.85 0.1 0.05	80°C (176°F)	CR-39
4	PEGDA EBDA 184	15 84.5 0.5	90°C (194°F)	POLYCARBONATE
5	PEGDA EBDA 184	50 49.5 0.5	50°C (122°F)	POLYCARBONATE
6	PEGDA DEG-BAC PEMA 184	17.5 70 13.5 2.5	81°C (178°F)	CR-39

Definition of terms: DEG-BAC: Diethylene Glycol Bisallyl Carbonate; PEGDA: Polyethylene Glycol Diacrylate; THFA: Tetrahydrofurfuryl Acrylate, EBDA: Ethoxylated Bisphenol A Diacrylate; PEMA: 2-Phenoxyethyl Methacrylate, 9008: Alkoxylated Trifunctional Acrylate, 9209: Alkoxylated Difunctional Acrylate Ester, 184: 1-Hydroxycyclohexyl Phenyl Ketone, TIN 1130: 2-Hydroxyphenyl Benzotriazole, TIN 292: Bis(1,2,2,6,6-Pentamethyl-4-Piperidinyl)Sebacate.

These polymeric matrices can be loaded with the photochromic additives. Preferred photochromic molecules for the practice of the present invention include spiro(indolino)naphthoxazines, spiro(indolino)pyridobenzoxazines, spiro(benzindolino)naphthoxazines, and octamethyl stilbene.

Several means are available for loading the photochromic additives into the polymeric matrices. For example, the photochromic additives can be added to the monomer formulation prior to polymerization, provided that the additives survive the conditions of polymerization. The matrix can be imbibed with the photochromic additives, either by slow diffusion, or by taking the matrix to a temperature above its glass transition temperature, then immersing it for a short time into a solution of the photochromic additives in a chemically inert solvent.

Alternatively, the matrix may be sprayed or spin coated with a solution of the photochromic additive, the solvent evaporated off, then the polymeric matrix may be heated to allow the photochromic additive thus deposited on the surface to diffuse inward, and eventually develop a gradient of concentration. The process of forming the matrix layer and addition of photochromic additives may be repeated several times in order to build up an overall thickness appropriate for the contemplated application.

The polymeric matrices described herein can be applied to optical products in many ways. For example, the polymeric matrix can be developed as a conformal layer bonded to the optical product via an interface region composed of an interpenetrating network. In another method of application of the polymeric matrix to the optical product, the polymeric matrix is produced in the form of a thin sheet which is adhesively bonded to the optical product of interest. In yet another method

of application of the polymeric matrix to the optical product, the polymeric matrix material bearing the photochromic additive may be formed as a solid powder, then suspended in a liquid in order to dip, spray, spin or brush coat the optical product. The matrix material will not dissolve in any solvent because it is cross linked. In yet another method of application of the polymeric matrix to the optical product, the matrix material may be partially polymerized to form a sticky, viscous material, loaded with the photochromic additives, dispersed in a carrier fluid, then dip, spray, spin or brush coated onto the optical product.

Still other embodiments will become immediately apparent to those skilled in the art upon reading this specification and the claims below. All patents, patent applications and other references cited herein, including priority applications, are incorporated by reference in their entireties.

What is claimed is:

1. A polymeric material comprising main chain ether groups or side chain alkoxylated groups, said polymeric material having a glass transition temperature of at least 125 °F and a cross link density of 2 to 8 moles per liter, and said polymeric material being effective as a carrier of photochromic additives.

2. The polymeric material of claim 1, wherein said polymeric material comprises one or more polymerized monomers selected from the group consisting of mono- or multi-functional acrylates or methacrylates.

3. The polymeric material of claim 2, wherein said monomers are selected from the group consisting of Bisphenol A derivatives of mono- or multi-functional acrylates or methacrylates; aromatic carbonates of mono- or multi-functional acrylates or methacrylates; aliphatic carbonates of mono- or multi-functional acrylates or methacrylates; and allyl and vinyl derivatives of mono- or multi-functional acrylates or methacrylates.

4. The polymeric material of claim 2, wherein said polymeric material comprises one or more polymerized monomers are selected from the group consisting of polyethylene glycol diacrylates, ethoxylated bisphenol A diacrylates, 2-phenoxyethyl methacrylates, alkoxylated trifunctional aliphatic acrylates, alkoxylated aliphatic diacrylate esters, tetrahydrofurfuryl acrylates, alkoxylated trifunctional acrylates, and alkoxylated difunctional acrylate esters.

5. The polymeric material of claim 1, wherein said cross link density ranges from 2.5 to 6 moles per liter.

6. The polymeric material of claim 1, further comprising a photochromic additive selected from the group consisting of spiro(indolino)naphthoxazines, spiro(indolino)pyridobenzoxazines, spiro(benzindolino)naphthoxazines, and octamethyl stilbene.

7. A resin formulation comprising one or more monomers which, when polymerized form a polymeric material comprising main chain ether groups or side chain alkoxylated groups, said polymeric material having a glass transition temperature of at least 125 °F and a cross link density of 2 to 8 moles per liter, and said polymeric material being effective as a carrier of photochromic additives.

8. The resin formulation of claim 7, further comprising a photoinitiator.

9. The resin formulation of claim 8, wherein said photoinitiator is selected from the group consisting of bisdimethoxybenzoyl trimethylpentyl phosphine oxide, 1-hydroxy cyclohexyl phenyl ketone, and 2-hydroxy, 2-methyl, 1-phenyl propane.

10. The resin formulation of claim 7, further comprising a thermal initiator.

11. The resin formulation of claim 10, wherein said thermal initiator is selected from the group consisting of organic peroxides, hydroperoxides, percarbonates, peracetates and azo derivatives.

12. The resin formulation of claim 11, wherein said thermal initiator is selected from the group consisting of benzoyl peroxide, 2,2′ azobisisobutyronitrile, and diisopropyl percarbonate.

13. The resin formulation of claim 7, further comprising an antioxidant.

14. The resin formulation of claim 13, wherein said antioxidant is selected from the group consisting of thiodiethylene bis(hydrocinnamide) and bis (1,2,2,6,6,-pentamethyl-4-piperidyl sebacate).

15. The resin formulation of claim 7, further comprising a photochromic additive.

16. The resin formulation of claim 15, wherein said photochromic additive is selected from the group consisting of spiro(indolino)naphthoxazines, spiro(indolino)pyridobenzoxazines, spiro(benzindolino)naphthoxazines, and octamethyl stilbene.

17. The resin formulation of claim 7, wherein said monomers are selected from the group consisting of mono- or multi-functional acrylates or methacrylates.

18. The resin formulation of claim 17, wherein said monomers are selected from the group consisting of Bisphenol A derivatives of mono- or multi-functional acrylates or methacrylates; aromatic carbonates of mono- or multi-functional acrylates or methacrylates; aliphatic carbonates of mono- or multi-functional acrylates or methacrylates; and allyl and vinyl derivatives of mono- or multi-functional acrylates or methacrylates.

19. The resin formulation of claim 17, wherein said monomers are selected from the group consisting of polyethylene glycol diacrylates, ethoxylated bisphenol A diacrylates, 2-phenoxyethyl methacrylates, alkoxylated trifunctional aliphatic acrylates, alkoxylated aliphatic diacrylate esters, tetrahydrofurfuryl acrylates, alkoxylated trifunctional acrylates, and alkoxylated difunctional acrylate esters.

20. The resin formulation of claim 7, wherein said cross link density ranges from 2.5 to 6 moles per liter.

21. A method of forming a polymeric material impregnated with a photochromic additive comprising:

providing a polymeric material comprising main chain ether groups or side chain alkoxylated groups, said polymeric material having a glass transition temperature of at least 125 °F and a cross link density of 2 to 8 moles per liter;

providing a photochromic additive;

incorporating said photochromic additive into said polymeric material.

22. The method of claim 21, wherein said polymeric material is provided by polymerizing a monomer formulation,and wherein said photochromic additive is incorporated into said polymeric material by adding the photochromic additive to the monomer formulation before it is polymerized.

23. The method of claim 21, wherein said photochromic additive is incorporated into said polymeric material by diffusing the photochromic additive material into the polymeric material.

24. The method of claim 23, wherein said photochromic additive is incorporated into said polymeric material by immersing it into a solution of the photochromic additives in a chemically inert solvent.

25. The method of claim 23, wherein said photochromic additive is incorporated into said polymeric material by spraying or spin coating the polymeric material with a solution of the photochromic additives in a chemically inert solvent.

26. The method of claim 21, wherein said photochromic additive is incorporated into said polymeric material by repeatedly providing a surface layer of polymeric material and subsequently incorporating said photochromic additive into said surface layer of polymeric material.

27. The method of claim 21, wherein said polymeric material with said incorporated photochromic additive is bonded to an optical product by an interfacial region composed of an interpenetrating network.

28. The method of claim 21, wherein said polymeric material with said incorporated photochromic additive is bonded to an optical product by an adhesive layer.

29. The method of claim 21, further comprising forming the polymeric material incorporating the photochromic additive as a solid powder, suspending the solid powder in a liquid, and applying the suspended powder to an optical product.

30. The method of claim 21, wherein said wherein the polymeric material incorporating the photochromic additive is provided by partially polymerizing the polymeric material; loading the partially polymerized

polymeric material with the photochromic additives; dispersing the loaded, partially polymerized polymeric material in a carrier fluid; and applying the carrier fluid with the dispersed, loaded, partially polymerized polymeric material onto an optical product.

31. The method of claim 21, wherein said photochromic additive is selected from the group consisting of spiro(indolino)naphthoxazines, spiro(indolino)pyridobenzoxazines, spiro(benzindolino)naphthoxazines, and octamethyl stilbene.

32. The method of claim 21, wherein said polymeric material comprises one or more polymerized monomers selected from the group consisting of mono- or multi-functional acrylates or methacrylates.

33. The method of claim 32, wherein said polymeric material comprises one or more polymerized monomers selected from the group consisting of Bisphenol A derivatives of mono- or multi-functional acrylates or methacrylates; aromatic carbonates of mono- or multi-functional acrylates or methacrylates; aliphatic carbonates of mono- or multi-functional acrylates or methacrylates; and allyl and vinyl derivatives of mono- or multi-functional acrylates or methacrylates.

34. The method of claim 32, wherein said polymeric material comprises one or more polymerized monomers selected from the group consisting of polyethylene glycol diacrylates, ethoxylated bisphenol A diacrylates, 2-phenoxyethyl methacrylates, alkoxylated trifunctional aliphatic acrylates, alkoxylated aliphatic diacrylate esters, tetrahydrofurfuryl acrylates,

alkoxylated trifunctional acrylates, and alkoxylated difunctional acrylate esters.

35. The method of claim 21, wherein said cross link density ranges from 2.5 to 6 moles per liter.

36. An optical product selected from the group consisting of uncorrected lenses, ophthalmic lenses, semifinished lens blanks, optical preforms, goggles, safety glasses, windows, and windshields, said optical product comprising the polymeric material of claim 1.

37. The optical product of claim 36, wherein said polymeric material comprises one or more polymerized monomers selected from the group consisting of mono- or multi-functional acrylates or methacrylates.

38. The optical product of claim 37, wherein said monomers are selected from the group consisting of Bisphenol A derivatives of mono- or multi-functional acrylates or methacrylates; aromatic carbonates of mono- or multi-functional acrylates or methacrylates; aliphatic carbonates of mono- or multi-functional acrylates or methacrylates; and allyl and vinyl derivatives of mono- or multi-functional acrylates or methacrylates.

39. The optical product of claim 37, wherein said monomers are selected from the group consisting of
polyethylene glycol diacrylates,
ethoxylated bisphenol A diacrylates,
2-phenoxyethyl methacrylates,
alkoxylated trifunctional aliphatic acrylates,
alkoxylated aliphatic diacrylate esters,
tetrahydrofurfuryl acrylates,
alkoxylated trifunctional acrylates, and
alkoxylated difunctional acrylate esters.

40. The optical product of claim 36, wherein said cross link density ranges from 2.5 to 6 moles per liter.

41. The optical product of claim 36, further comprising a photochromic additive selected from the group consisting of spiro(indolino)naphthoxazines, spiro(indolino)pyridobenzoxazines, spiro(benzindolino)naphthoxazines, and octamethyl stilbene.

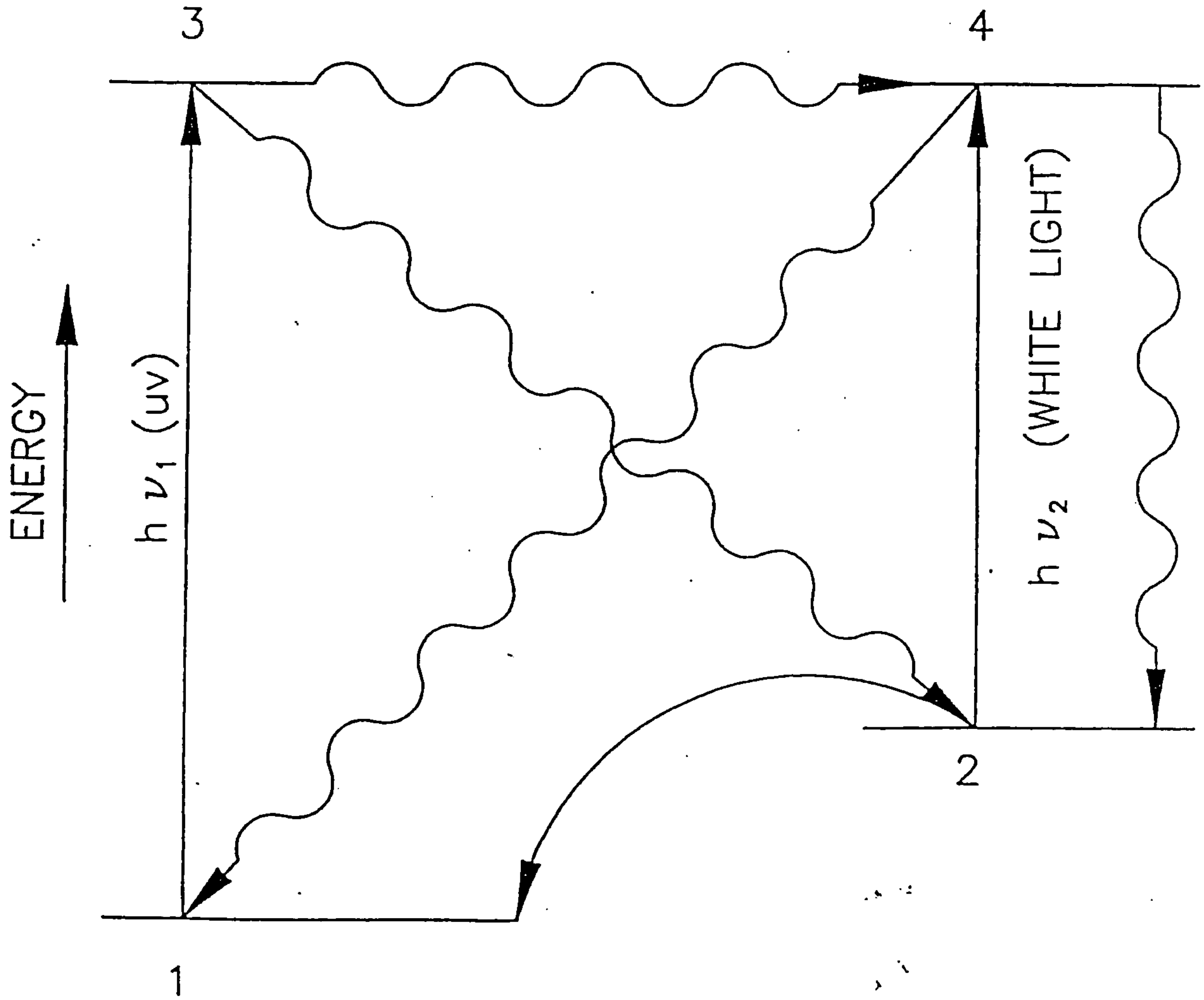

FIGURE 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/13302

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :Please See Extra Sheet.
US CL :428/156; 524/89, 92, 559, 601, 604; 526/313, 314, 318.1; 528/196
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/156; 524/89, 92, 559, 601, 604; 526/313, 314, 318.1; 528/196

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,021,196 A (CRANO ET AL) 04 June 1991, columns 21-25.	1-41
A	US 4,936,995 A (KWIATKOWSKI) 26 June 1990.	1-41
A	US 4,909,963 A (KWAK ET AL) 20 March 1990.	1-41
A	US 4,544,572 A (SANDVIG ET AL) 01 October 1985.	1-41
A	US 4,286,957 A (LE NAOUR-SENE) 01 September 1981.	1-41

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
21 OCTOBER 1996	06 NOV 1996

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/13302

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/13302

A. CLASSIFICATION OF SUBJECT MATTER:
IPC (6):

B32B 3/00; C08F 18/24, 22/14, 112/14, 116/12, 120/20, 122/14, 212/14, 216/12; C08G 64/02, 64/04; C08K 5/34

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING
This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

This application contains claims directed to more than one species of the generic invention. These species are deemed to lack Unity of Invention because they are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for more than one species to be searched, the appropriate additional search fees must be paid. The species are as follows:

There are two distinct species which do not share the same technical features of invention represented when the "alkoxylated group" is within the polymer chain as opposed to when it is pendant on the polymer chain. These represent two different and distinct classes of polymers which do not share reactivities or properties.